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Physical and electrical properties of flash memory devices with nickel oxide(NiO_2) charge trapping layer

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ABSTRACT

In this study, we proposed a metal-oxide high-k-oxide-silicon (MOHOS) memory device using a nickel oxide film as the charge trapping layer, and studied the effect of post-deposition rapid thermal annealing (RTA) on the physical and electrical properties. The physical properties were investigated via multiple material analysis techniques such as X-ray diffraction and atomic force microscopy. The optimal annealing temperature for depositing the charge trapping layer was determined through a thorough investigation of the memory window, program/erase (P/E) cycle, crystalline structure, and material composition. Compared to the as-deposited NiO_2 film, a MOHOS-type memory device annealed at 900 °C in a nitrogen atmosphere exhibited improved memory characteristics, in terms of a larger window in the capacitance-voltage hysteresis, better data retention (lower charge loss of 11%), faster program and erase cycles, and endurance characteristics (10^4 P/E cycles) without any significant drift in the flat band voltage. Therefore, the MOHOS memory device with a NiO_2 trapping layer is a very promising candidate for future memory device applications.

1. Introduction

Nonvolatile memory (NVM) devices are extensively used in compact data storage and integrated memory modules for several microcontroller applications. Memory devices with higher density, faster operation, and lower power consumption are essential for next generation nonvolatile flash memory devices [1–4]. Furthermore, NVM devices employing discrete charge traps have attracted attention as a promising alternative to the conventional floating gate (FG) memory, which is expected to have longer charge retention and better endurance characteristics [5–8]. However, the storage charge in the nitride trapping layer will be easily lost because of the formation of a large number of defects in the tunneling oxide after repeated program/erase (P/E) cycles or through the direct tunneling current. Therefore, to ameliorate the P/E speed, a high dielectric constant (high-k) charge trapping layer grown on top of the SiO_2 film is used to maintain the P/E speed and reliability simultaneously [9–13]. Different kinds of nanocrystals (NCs) and blocking oxide layers for NC–NVM devices have been investigated [14–17]. NCs of Si, Ge, Ni, Pt, and Au have been the major candidates for the charge-storage nodes. To overcome the quantization limitations of semiconducting dots and to facilitate higher carrier confinement, metallic NCs with a high density of states and large work function have been the subject of several studies. In addition, according to some reports, Ti-doped high-k materials can improve the memory device performance, such as increasing the k value and making the electric field across the tunneling oxide more efficient [17–20].

Nickel oxide is widely used for batteries, fuel cells, and solar cells because of its desirable physical and chemical properties [21–27]. Nickel oxide seems a promising candidate for NVM devices owing to its wide band gap of 3.6 eV. Sato et al. have already demonstrated an application of nickel oxide for resistive random access memory (RRAM) with excellent performance and reliability.

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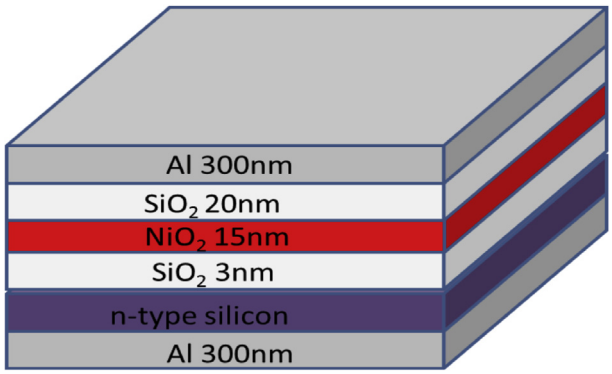

Fig. 1. NiO_2 flash memory device structure.

An initial forming voltage as low as 2 V was achieved using a thin NiO film, and the reset current was lower than 100 μA [28]. In this study, we proposed a metal-oxide high-k-oxide-silicon (MOHOS) memory device using a nickel oxide film as the charge trapping layer, and studied the effect of post-deposition rapid thermal annealing (RTA) on the electrical and physical properties. Electrical measurements, including the capacitance-voltage (C-V) hysteresis and data storage capabilities, were performed on the annealed samples in order to examine the performance. The material properties were investigated via multiple material analysis techniques such as X-ray diffraction (XRD) and atomic force microscopy (AFM). The optimal annealing temperature for depositing the charge trapping layer was determined through a thorough investigation of the memory window, P/E cycle, crystalline structure, and material composition.

2. Experimental

The MOHOS memory structure using the NiO_2 film as a charge trapping layer was fabricated on 4-inch n-type Si (100) wafers. After standard RCA cleaning, a 3-nm-thick SiO_2 layer was thermally grown using a dry oxidation furnace system at 850 °C. Subsequently, a 15-nm thick NiO_2 trapping layer was deposited by radio frequency (RF) sputtering using a pure nickel target in a diluted oxygen atmosphere ($Ar/O_2 = 20/5$) with a RF power of 150 W. Next, the wafers were annealed at various temperatures (600 °C, 700 °C, 800 °C, and 900 °C) by RTA in a nitrogen atmosphere for 30 s to form the NiO_2 charge trapping layer. Then, a 20-nm thick SiO_2 film was deposited as a blocking oxide layer by plasma-enhanced chemical vapor deposition (PECVD) at 300 °C. Subsequently, a 300-nm thick aluminum film was deposited using a thermal evaporator and patterned using lithography and wet etching. Finally, a 30-nm thick aluminum layer was deposited on the back side of the Si wafer structures, and this was followed by a hydrogen sintering process at 400 °C for 30 min. The MOHOS memory device was fabricated and the device structure is shown in Fig. 1.

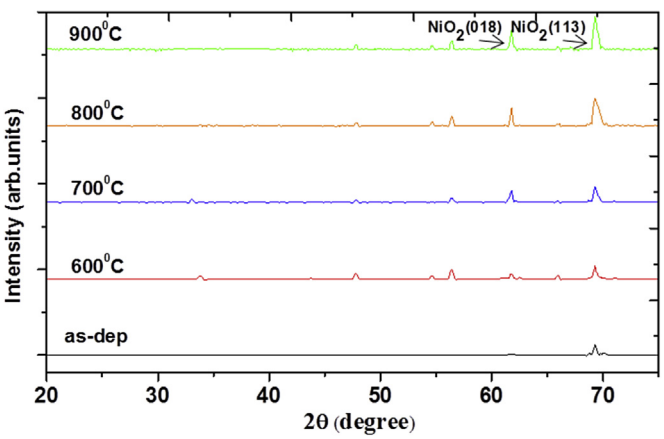

Fig. 2. XRD of the as-deposited film and the films after RTA annealing treatment at 600 °C, 700 °C, 800 °C, and 900 °C.

Material analyses of the NiO_2 trapping layer were performed by XRD and AFM to examine the relation between the electrical characteristics and the material properties. The XRD spectra were obtained at a grazing incidence of CuKα (k = 1.542 Å) radiation. The system used a grazing incidence angle (θ = 0.5) over the diffraction angle range (2θ) 20–75°. The low penetration of the incident X-rays under this condition results in good crystalline structures and increases the surface selectivity.

Further, the surface morphologies of the NiO_2 film were monitored using AFM (Veeco, model D5000) operated in the tapping mode using an Applied Nano silicon tip with a 50 N/m spring constant.

3. Results and discussion

To investigate the crystalline structure of the NiO_2 films, XRD was used to analyze the as-deposited sample and the samples annealed at 600 °C, 700 °C, 800 °C, and 900 °C. As shown in Fig. 2, the XRD spectra presented two major diffraction peaks, NiO_2 (113) at $2\theta = 69.1°$ and NiO_2 (018) at $2\theta = 62.4°$. The intensity of the diffraction peak of NiO_2 (113) was the strongest of all peaks. It can be seen that the higher the annealing temperature was, the stronger the diffraction peak of NiO_2 film became, suggesting a preferential orientation of the crystalline structure. The strongest intensities and crystallization phases appeared for the sample annealed at a high temperature of 900 °C. Higher annealing temperatures could reduce defects, interface states, and improve dangling bonds to yield stronger Ni-O bonding by repairing the oxygen vacancies. This may be due to a sufficient thermal budget at higher temperature that enables the occurrence of a complete reaction and suppression of the formation of the silicate layer at the interface between SiO_2 and NiO_2 to facilitate formation of a well-crystallized structure [29,30].

To understand the chemical reaction of the films at different annealing temperatures, the O 1s XPS spectra is as shown in Fig. 3(a) with their appropriate peak curve-fitting lines corresponding to chemical states. In three sets of spectra, each fitting peak is assumed to follow the general shape of the Gaussian function. The low energy at 530.5 eV is attributed to O in NiO_2. The intermediate energy at 531.8 eV is attributed to interfacial O atoms in Ni silicate ($NiSixOy$). The high energy at 533.2 eV is attributed to O in SiO_2. For the as-deposited film, the Ni silicate intensity is strong but the NiO_2 intensity is weak. As the annealing temperatures increased, the silicate intensity decreased, but the NiO_2 intensity increased, indicates that the NiO_2 structure became stronger as the annealing temperature increased to 900 °C. Moreover, the Ni 2p XPS spectra of NiO_2 film are shown in Fig. 3(b), and the binding energy of the peak position of Ni $2p_{3/2}$ and Ni $2p_{1/2}$ for the as-deposited sample can be found at 853.54 eV and 871.03 eV, suggesting a poor structure due to the hydroxide formation after exposure to an air ambient. The Ni 2p peak shifted toward a higher binding energy as increasing annealing temperature to 900 °C, indicating that stronger bonds were formed during high temperature annealing.

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